Abstract

Due to the limited availability of products derived from oil fields and petroleum, biobased materials are essential for building a low-carbon society. Researchers are trying to reduce the consumption of non-renewable resources produced by synthetics by utilizing alternative materials such as natural biopolymers. The relationship between polymer structure and physical properties is critical in materials design. Engineering plastics from biomolecules are well suited for such materials in terms of available volume and cost. Development of such high-performance and high-performance biobased polymers is very important for building a sustainable low-carbon society. In this paper, we focus our research on the synthesis of high-performance polyureas from bio-based furan, aromatic, and heterocyclic compounds. The development of such high-performance biobased polymers is essential for the realization of a sustainable low-carbon society. Important and interesting results obtained through this research are summarized in the following parts.

In Chapter 2, syntheses of polyureas with furan as the main chain using AMF and the addition of sol-gel transition, self-healing, and cross-healing functionalities via the Diels-alder reaction. Bio-based polyureas with furan rings in the main chain were synthesized from 2,5-bis(aminomethyl)furan in DMAc and various diisocyanate compounds via a one-step solution polymerization route. The physical properties of the polyurea samples were determined by H-nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy. Thermophysical properties of polyurea samples have been investigated by differential scanning calorimetry and thermogravimetric analysis. A reversible DA reaction between furan and maleimide was used to successfully crosslink furan polyurea and bismaleimide. The polyurea gel exhibited repair properties based on dynamic bond recovery and was found to adhere to the fracture site at 60°C. Reversible sol-gel transition based on DA reaction provided temperature-responsive gels.

In Chapter 3, aromatic diamine 2-(4-aminophenyl) ethylamine (4APEA) was produced by fermentation using genetically engineered Escherichia coli and its condition optimization was evaluated. The fermented 4APEA was purified from the medium and polymerized with methylene diphenyl diisocyanate and hexamethylene diisocyanate to produce polyureas. 10% weight loss temperature (T_{d10}) results were above 276°C, respectively, which is comparable to other heat-resistant aromatic temperatures of other thermostable aromatic polyureas. This study is the first to synthesize polyureas from microbial aromatic diamines. Their excellent thermal stability will be useful in the industrial production of heat-resistant polymeric materials.

Chapter 4 presents the synthesis of functional polymers that promote degradability by imparting photo-induced hydrophilicity to biobased polyureas. Itaconic acid, which can be produced from biological sources, is used to synthesize diamine oligomers. We will then synthesize various polyureas by reacting them with typical diisocyanates and compare them with biogenic polyureas we have prepared so far and evaluate the structure-property relationship. The preliminary review will introduce the synthesis of new itaconic acid-derived polyurea and the evaluation of its thermophysical and photo responsiveness properties.

As conclusions, the development of biologically derived polyureas showed good thermal and mechanical performance. The introduction of a furan ring into the main chain was accompanied by thermo-reversible reactions, enabling self-healing properties and controlled sol-gel transition. These polyurea materials are not only expected to be applied to temperature-responsive actuators, self-healing agents, and heat-resistant coatings, but also to help build a sustainable green society.

Keywords：bio-based monomer, polyurea, aromatics, self-healing, stimulus responsiveness